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Synthesis, Structure, and Reactivity of a Zirconocene Complex of Cyclobutene

by

Richard A. Fisher and Stephen L. Buchwald*

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Synthesis, Structure, and Reactivity of a Zirconocene

Complex of Cyclobutene

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ABSTRACT

The first structurally characterized transition metal complex of cyclobutene is described. The complex is formed by the elimination of methane from cyclobutyl(methyl)zirconocene with subsequent trapping by trimethylphosphine. The reactivity of the complex with unsaturated organic molecules and its X-ray crystal structure are reported.

Handwritten notes:
Synthesis, Structure, and Reactivity, Zirconocene, Cyclobutene, Main Group Metallacycles, Solid State, Organometallics, Sulfur



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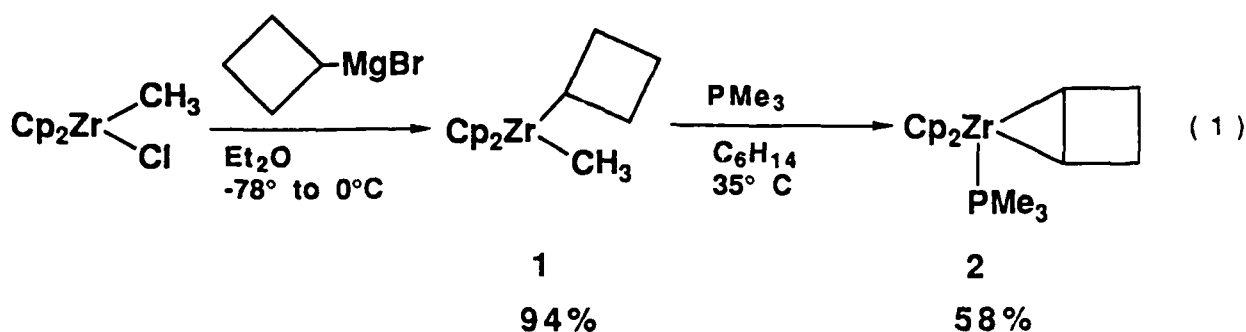
Synthesis, Structure, and Reactivity of a Zirconocene Complex of Cyclobutene

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Early transition metal complexes of arynes and alkynes have been the subject of numerous recent publications.² Interest in these complexes stems from their novel structures and their use as intermediates in the selective synthesis of organic molecules. Olefin complexes of early transition metals have not been studied to the same extent, in part due to difficulties encountered in their synthesis and isolation. Until very recently, the only structurally characterized group 4 metal complex of an olefin was the $\text{Cp}^*_2\text{Ti}(\eta^2\text{-ethylene})$ complex reported by Bercaw and coworkers.³ Renewed interest in the chemistry of alkene complexes of the group 4 metals has resulted in several recent reports of alkene complexes of titanium, zirconium, and hafnium.⁴ In this communication, we report the synthesis, structure, and reactivity of a zirconocene complex of cyclobutene. This represents the first structurally characterized group 4 metal complex of a cyclic olefin, and the only structurally characterized transition metal complex of cyclobutene.⁵

Treatment of ethereal solutions of zirconocene(methyl) chloride with cyclobutylmagnesium bromide at -78°C , followed by warming to 0°C , cleanly forms cyclobutyl(methyl)zirconocene, which can be isolated as a thermally sensitive waxy yellow solid in ca. 90% yield. Addition of excess trimethylphosphine to hexane solutions of **1** and warming to 35°C for 12 h, results in the elimination of methane and the formation of the cyclobutene complex as its trimethylphosphine adduct, **2** (~85 % by ^1H NMR). Partial precipitation of the product occurs



during the course of the reaction which greatly facilitates the isolation of **2**. Recrystallization from hexanes/ether (10:1) affords pure **2** as a thermally sensitive crystalline orange solid.

Complex **2** was characterized by single crystal X-ray diffraction and the ORTEP, along with selected bond distances and angles, is shown in figure 1.⁶ The gross structural features of the zirconocene fragment are in accord with those of previously characterized zirconocene complexes.^{2i-k, 4b,c} The atoms of the cyclobutene ring are essentially planar with no deviations

Figure 1

Figure 1. Molecular structure of **2**. Selected bond lengths (Å): Zr-C(1) 2.333(9); Zr-C(2) 2.334; C(1)-C(2) 1.49(1); C(2)-C(3) 1.52(1); C(3)-C(4) 1.55(1); C(1)-C(4) 1.52(1); Zr-P 2.680(3). Selected bond angles (°): C(1)-Zr-C(2) 37.2(3); P-Zr-C(1) 111.8(2); C(1)-C(2)-C(3) 89.9(9); C(2)-C(3)-C(4) 89.9(7); C(3)-C(4)-C(1) 89.0(7); C(4)-C(1)-C(2) 92.3(7).

greater than 0.05 Å; the internal bond angles are 90°. A notable lengthening of the C(1)-C(2) bond distance relative to free cyclobutene⁷ is observed, indicating this bond possesses primarily single bond character. The dihedral angle between the plane of the four-membered ring and the ligands in the plane of the wedge (defined by Zr, P, C(1), and C(2)) is 122.7°. These two structural features indicate that substantial backbonding from the metal d orbitals to the π^* ligand orbitals is occurring, and is consistent with the representation of **2** as a zirconacyclop propane.

Complex **2** undergoes insertion reactions with a variety of unsaturated groups to afford good yields of the novel bicyclo [3.2.0] metallacycles as shown in Scheme I. Nitriles

Scheme I

are conveniently coupled by direct treatment of solutions of **1**, prepared *in situ*, with a slight excess of nitrile followed by heating to 40° C; no trimethylphosphine is required. The cyclobutene complex, **2**, reacts rapidly with one equivalent of acetone to provide a species

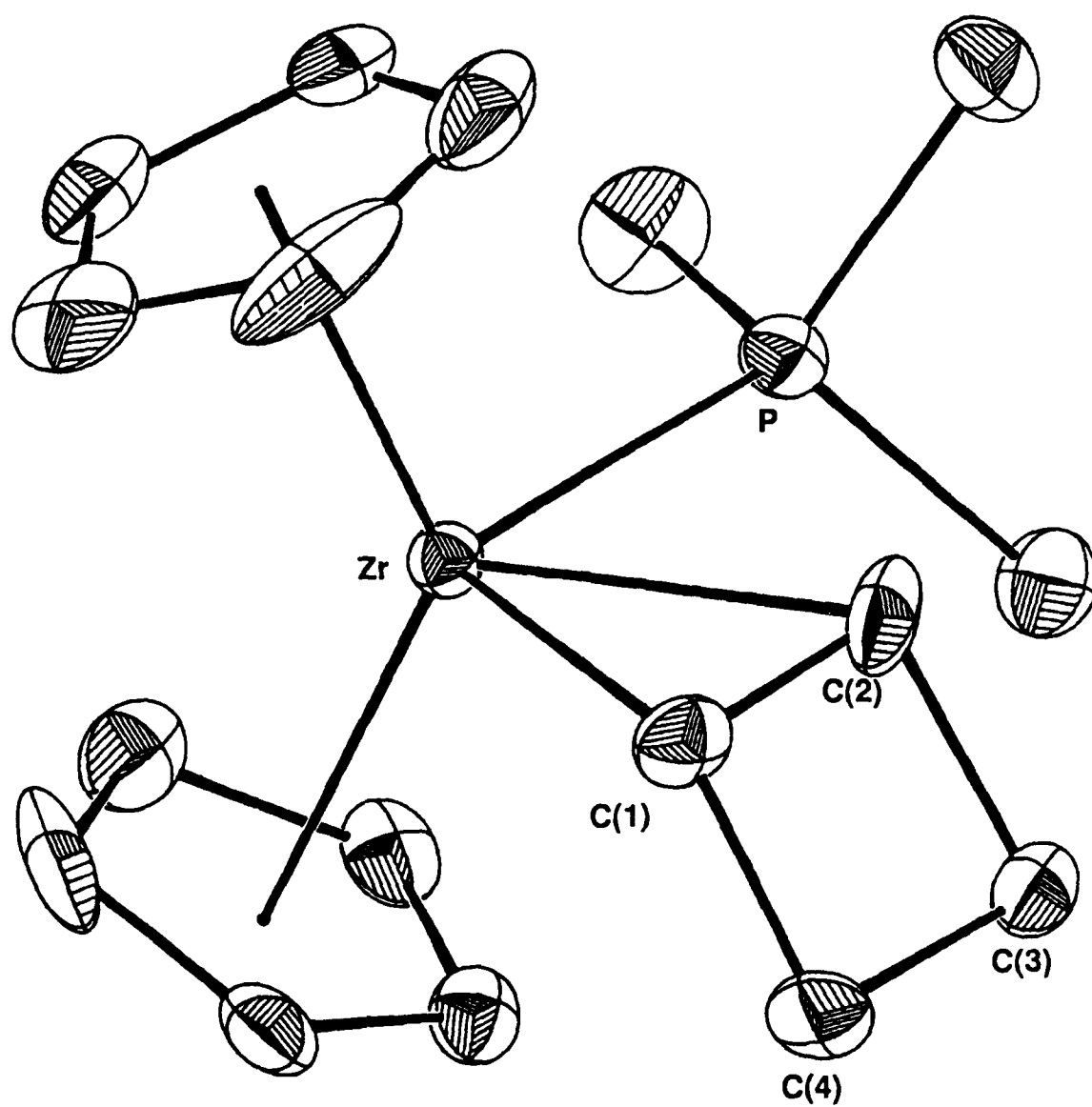
whose ^1H and ^{13}C NMR are consistent with structure 3. Compound 3 is unstable to removal of solvent and attempts to isolate it from the reaction mixture have thus far been unsuccessful. Alkynes react reversibly with 2 to yield an inseparable mixture of the desired insertion product 4 and the metallacyclopentadiene 5. Treatment of mixtures of 4 and 5 with an excess of alkyne converts 4 into 5. Complex 2 undergoes a rapid reaction at room temperature with two equivalents of *tert*-butylisocyanide to provide the novel double insertion product 6. Treatment of 2 with less than two equivalents of the isocyanide results in partial conversion to 6; the mono insertion product has not been observed in the reaction mixture.

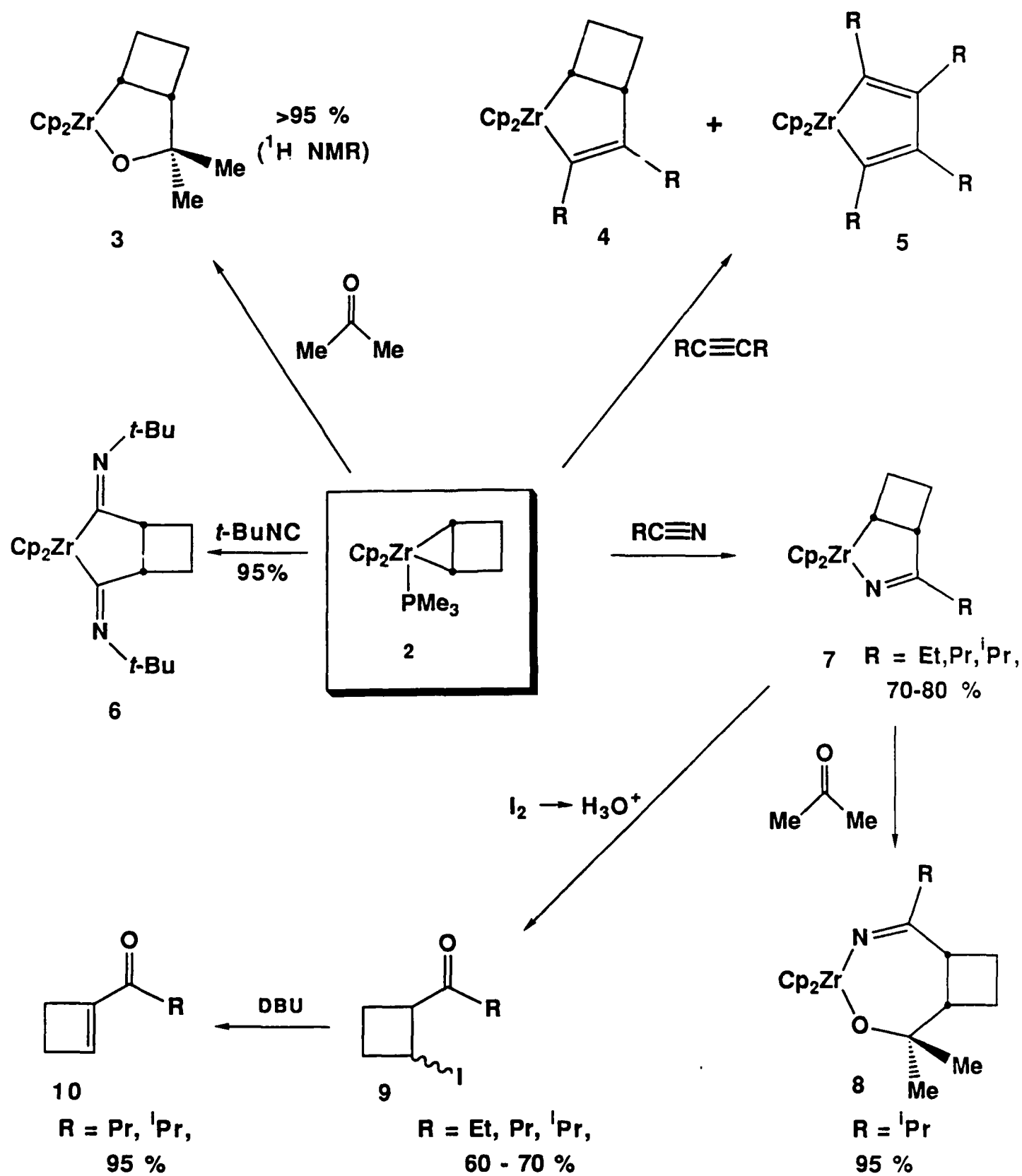
The azametallacycles 7 formed in the nitrile coupling reactions serve as useful intermediates for the further functionalization of the cyclobutane ring. Compound 7c cleanly inserts one equivalent of acetone to give the metallacycle 8. The conversions of 2 to 6 and 2 to 8 (via 7) represent rare examples of the formation of vicinal carbon-carbon bonds in the reaction of a cycloalkene. More generally, iodinolysis of the azametallacycles provides good isolated yields of the α -iodoacylcyclobutanes 9 as single diastereomers.⁹ Although the relative stereochemistry of the β -iodo ketones has not been unambiguously determined, spectroscopic evidence suggests that the iodo and acyl groups are *trans*. These β -iodo-ketones can be readily dehydrohalogenated by treatment with DBU in chloroform to form cyclobutenyl ketones, 10, in high yield.¹⁰

Further investigations of the diverse reactivity of 2 as well as investigations into the chemistry of other alkene complexes of group 4 metals are ongoing in our laboratory.

Acknowledgement. We gratefully acknowledge the National Institutes of Health (GM 34917), Eli Lilly, and, in part, the Office of Naval Research for their support of this work. We would also like to thank Dr. W. M. Davis of the MIT X-Ray Diffraction Facility for his crystallographic assistance, and the U. S. Department of Energy (Grant No. DE-FG05-86ER-75292) for funding for the Rigaku AFC6R.

Supplementary Material Available: Experimental section containing the preparation and spectroscopic characterization of compounds; crystallographic data and procedures, ORTEP diagrams of **2**, bond distances and angles, tables of final positional and thermal parameters, and tables of structure factors . Ordering information is given on any current masthead page.





Footnotes and References:

1. Camille & Henry Dreyfus Teacher-Scholar Awardee, 1989-94; American Cancer Society Junior Faculty Research Awardee 1987-89; Eli Lilly Grantee 1988-90; Alfred P. Sloan Research Fellow, 1988-90; Union Carbide Innovation Recognition Program Awardee, 1989.

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6. Single crystals of **2** were grown from a 10:1 hexane: ether solution at -40°C . A suitable crystal (0.25 mm X 0.15 mm X 0.18 mm) was mounted on a glass fiber under a cold N_2 stream. Data were collected at -77°C on an Enraf-Nonius CAD-4 Diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation, $\lambda = 0.7169\text{\AA}$. Monoclinic, space group $\text{P}2_1/\text{n}$, $a = 8.182(4)\text{\AA}$, $b = 15.610(3)\text{\AA}$, $c = 12.384(6)\text{\AA}$; $\beta = 95.68(2)^{\circ}$. $V = 1574(2)\text{\AA}^3$; $Z = 4$; $d(\text{calcd}) = 1.484\text{ g/cm}^3$. A total of 2192 data ($I > 3\sigma(I)$) were collected using an ω - 2θ scan to 2θ of 55.2° , reflection to parameter ratio = 12.7. The structure was solved by the Patterson method and refined without complications. Anisotropic refinement of all non-hydrogen atoms by full matrix least squares (fixed hydrogen parameters, $d_{\text{C-H}} = 0.95\text{\AA}$) resulted in $R = 0.060$ and $R_w = 0.070$. A full report of the data collection and structure solution and refinement is given in the supplemental material.
7. The carbon-carbon double bond and the average carbon-carbon single bond of cyclobutene have been determined by electron diffraction in the gas phase as $1.33 \pm 0.04\text{\AA}$, and $1.54 \pm 0.01\text{\AA}$ respectively^{8a,b}. (a) Goldish, E.; Hedberg, K.; Schomaker, V.; *J. Amer. Chem. Soc.* **1956**, *78*, 2714. (b) Dunitz, J. D.; Schomaker, V. *J. Chem. Phys.* **1952**, *20*, 1704.
8. Similar reactivity and difficulties have been previously observed in a related system.^{3a,b}
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